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Degradation of the disazo acid dye by the sulfur-containing amino acids of wool fibers

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Abstract

In order to examine the color change of the disazo acid dyeings on wool fibers, C.I. Acid Blue 113 having disazo groups within the molecular structure was used and its characteristics of the color change were studied. The dye degradation was attributed to the reducing effect of the sulfur-containing amino acids within the wool fibers. The degraded moiety of the disazo dye was analyzed using an LC/MS. The mass spectrum showed that the mass of 326.1 corresponded to the dye moiety having monoazo group, which was formed by a reductive degradation of the disazo dye. From the model studies using cystine and cysteine, it was also found that the formation of the monoazo moiety was attributable to the reducing effect of the cystine and the cysteine.
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Keywords: Reductive degradation; Reducing effect; Disazo acid dye; C.I. Acid Blue 113; Wool; Amino acid; Cystine; Cysteine

1. Introduction

There are many kinds of dyes being used in the textile industries. With the reactive dyes and disperse dyes, the acid dyes are one of the most widely used commercial dyes in terms of their quantity of production and consumption [1]. Owing to the wide range of commercially available acid dyes, the acid dyes are commonly classified into several groups in terms of dyeability and chemical structure. In the case of dyeability, they are divided into three groups, namely levelling, half-milling and milling types. The levelling dyes having low molecular weight exhibit low substantivity, very good migration and levelling properties but poor wet fastness. In contrast, large molecular weight dyes, the milling dyes, display low migration and non-levelling properties but good wet fastness [2–4].

In the aspect of the chemical structure, the acid dyes are mainly classified into three groups, which are azo, anthraquinone and triphenylmethane types. Azo dyes are the largest representative among the several chemical classes of dye to which non-metallized acid dyes belong. Azo dyes are also classified into the two subgroups of monoazo and polyazo types. The polyazo acid dyes contain more than one azo group and they are commonly diszao types having two azo groups in their molecular structures. Compared to the monoazo dyes, the disazo dyes provide higher substantivity towards the fiber substrates and better fastness as well as deep shade of color could be achieved. However, the color changing problems of the disazo dyes occurred during wool dyeing process. When the wool fibers are dyed with disazo acid dyes at high temperature, sometimes the shade of the dyed substrates could be changed from original dark shades of blue or black to reddish color

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[5,6]. This observed property is accelerated in alkaline condition rather than in acidic condition.

In this study, in order to investigate the color changing properties of disazo acid dyes in wool dyeing, C.I. Acid Blue 113 was selected. This dye is one of the representative disazo types which are generally used in wool dyeing to obtain deep shade of navy blue color. In this context, the color changing behavior was studied in terms of the dye degradation due to the reducing effects of the sulfur-containing amino acids within the wool fibers. In addition, the degraded moiety of the dye was analyzed and characterized using an LC/MS.

2. Experimental

2.1. Materials

The scoured wool and silk fibers were prepared. The disazo acid dye used was C.I. Acid Blue 113 and its chemical structure is shown in Fig. 1. In order to purify, the dye was dissolved with *N*,*N*-dimethylformamide and then the dye solution was filtered to remove any undissolved impurities. Diethyl ether was slowly added to the filtrates to precipitate and recrystallize the dye molecules. The purified dye was dried.

The first grade reagents of cystine, cysteine and methionine were used without purification.

2.2. Dyeing

The wool and silk fibers (2.0 g) were dyed with C.I. Acid Blue 113 (1.0% owf) in the buffer solutions of pHs 5, 7, 9 and 11 at 95 °C for 180 min. The liquor ratio was 1:20. At the end of dyeing, the dyed fibers were washed in tap water and then dried in the open air.

2.3. Measurement of color

The colorimetric data of dyeings were obtained using a *Datacolor SF 600 plus* spectrophotometer interfaced to a PC. Measurements were taken with the specular component of the light excluded and the UV component included, using illuminant D_{65} and 10° standard observer. The UV/vis spectra of the dye solutions were measured using a *Shimadzu UV/VIS spectrophotometer UV-2100*.

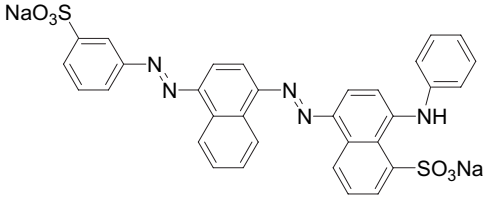


Fig. 1. A structure of C.I. Acid Blue 113.

2.4. Dye extraction

To determine the dye degradation, the dyes were extracted from the dyed substrates using 25% pyridine aqueous solution at 95 °C for 3 h.

2.5. Model experiments with the sulfur-containing amino acids

To investigate whether the sulfur-containing amino acids within the wool fibers could influence the degradation of the disazo acid dye, three amino acids were used as the model compounds, namely L-cystine, L-cysteine and L-methionine (Fig. 2). These amino acids (0.1 g) were added into the acid dye solutions (100 ml) of pH 9 and 11. The solutions were heated up to 95 °C and the treatments were maintained for 60 min.

2.6. Analysis of the degraded dye moiety using LC/MS

To analyze the dye degradation, the LC/MS (Hewlett Packard Series 1100) was used. The prepared solutions containing the degraded dye moieties were injected into the LC/MS and the mass spectra of the samples were then determined. The composition of the mobile phase was a mixed solution (water and methanol, 10:90) and its flow rate was 0.5 ml/min. The stationary phase was the C18 column (HP Eclipse® XDB-C18, 4.6 × 150 mm, 3.5 μm). The mass spectra were obtained at API-ES negative mode and the fragment voltage was 100.

3. Results and discussion

3.1. Color change of C.I. Acid Blue 113 in wool dyeing

As mentioned earlier, the blue disazo acid dyes have met undesirable problems when the dyes were subjected to the wool dyeing. The blue color of the dyed samples may change to reddish shade. This observation is accelerated in alkaline condition rather than in acidic condition. In this study, to investigate the color changing properties, the wool fibers were dyed with C.I. Acid Blue 113 that is a disazo type. The dyeings were carried out in various pHs of 5, 7, 9 and 11. The colorimetric data of the dyeings are represented in Table 1 and Fig. 3. Table 1 and Fig. 3 show that the original color of navy blue was achieved in acidic

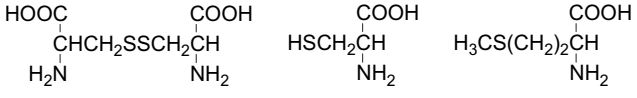


Fig. 2. Sulfur-containing amino acids.

Table 1
Colorimetric data of wool dyeings with C.I. Acid Blue 113 at various pHs

pH	L^*	a^*	b^*
5	19.02	8.49	−19.97
7	21.20	6.76	−18.15
9	59.70	24.42	35.82
11	61.13	20.56	31.83

Colorimetric data represented as L^* − lightness and a^*, b^* − chroma coordinates in CIELAB color space.

and neutral dyeing conditions but in alkaline baths its shades were changed to the reddish orange colors. The data in Fig. 3, namely the *a*,*b* plots for the dyeings, clearly show the direction of color changes. In the coordinates of the chromacity components (*a*,*b*), the changes occurred in the direction of decreased blue component.

In general, most of the acid dyes are applied in acidic dyeing bath. However, because the disazo acid dyes are considered as the milling type dyes that are usually dyed in weak acidic or neutral conditions, the color changes of the disazo acid dyeings could have occurred. Even though the color changes are not significant levels in those conditions, it might be noticeable effects to the practical dyeings and could negatively influence on the final dyeing products [6]. In this context, in order to clarify the degradation mechanism and to accelerate the degradation of the dyes, the experiments were carried out in alkaline conditions.

3.2. Analysis of the degraded dye moiety

To analyze the degraded dye moiety, the extraction of the dyed wool fibers was conducted using 25% of pyridine aqueous solution. Fig. 4 shows the UV/vis spectra of the original C.I. Acid Blue 113 and its degraded moiety extracted from the wool dyeings. This absorbance behavior represents the marked color changes from blue to reddish orange. As shown in Fig. 4, the maximum absorption wavelength (λ_{max}) of C.I. Acid Blue 113 was 580 nm. However, the extracted dye moiety from the wool dyeings under alkaline conditions showed its maximum absorption wavelength of 450 nm. C.I. Acid Blue 113 is a disazo type containing two azo groups that are relatively susceptible to alkalis. Thus, it is assumed that one of the two azo groups was degraded and its corresponding moiety behaved to be like monoazo acid dyes.

To verify this finding, the extracted dye moiety from wool dyeing was analyzed using an LC/MS. In the 4.3 min of retention time a colored material was showed up in HPLC and its fragment was subsequently injected to the mass analyzer. The resulting mass spectrum is shown in Fig. 5. In Fig. 5, the *m*/*z* 326.1 was predominantly detected. Thus, it was obvious that the mass of 326.1 was the moiety having one azo group which was formed by a reductive degradation of the

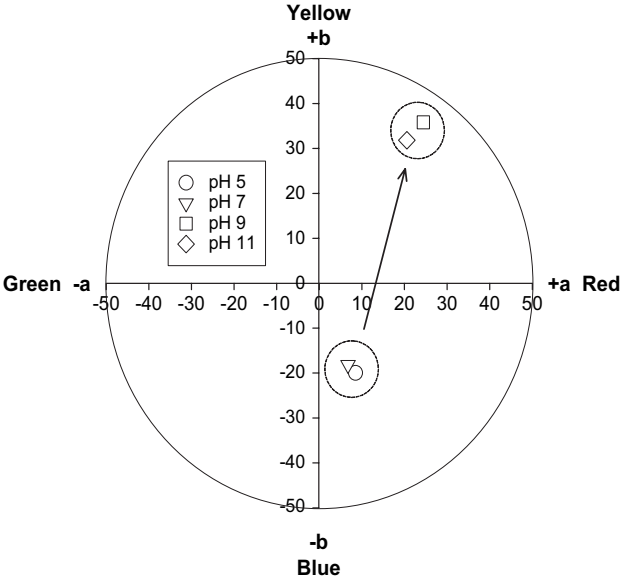


Fig. 3. Color coordinates of wool dyeings with C.I. Acid Blue 113 at various pHs.

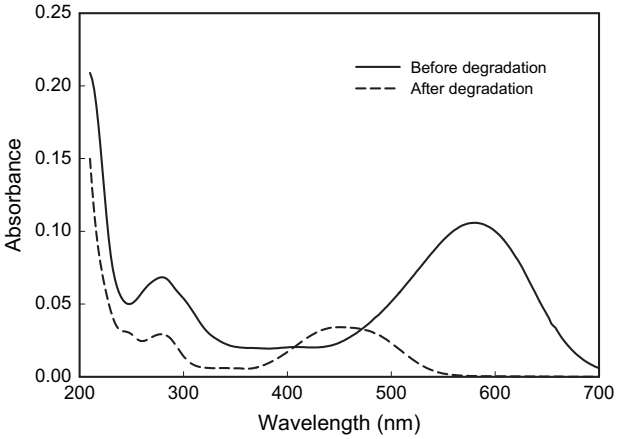


Fig. 4. The UV/vis spectra of original C.I. Acid Blue 113 and its degraded moiety extracted from wool dyeings.

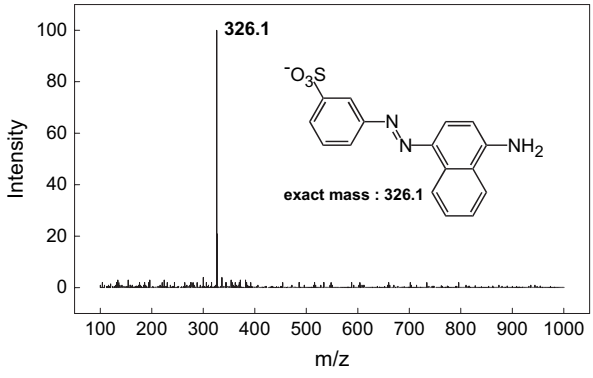


Fig. 5. The mass spectrum of the degraded dye moiety extracted from wool dyeing.

Table 2
Colorimetric data of silk dyeings with C.I. Acid Blue 113 at various pHs

pH	L^*	a^*	b^*
5	27.85	8.91	−25.90
7	28.74	8.76	−24.97
9	27.10	8.93	−25.71
11	29.16	8.35	−26.39

Colorimetric data represented as L^* − lightness and a^*, b^* − chroma coordinates in CIELAB color space.

disazo groups in the dye molecule. Because the degraded dye moiety still has one azo group, it shows the color of reddish orange to be like other monoazo dyes.

3.3. Color change of C.I. Acid Blue 113 in silk dyeing

An important finding was that the other protein fiber, silk, imparted little color change to the dyeings with C.I. Acid Blue 113. In other words, the specific components are present in the wool fiber molecules, which could cause the disazo dyes to degrade. Furthermore, this effect could be accelerated in alkaline conditions.

To study this property, the silk dyeing was conducted under the same condition as the wool dyeing. The silk fibers were dyed with C.I. Acid Blue 113 using the buffer solutions of pHs 5, 7, 9 and 11 at 95 °C for 180 min. As shown in Table 2 and Fig. 6, the color change was not observed in the silk dyeings even in alkaline conditions, which proposed different dyeing properties compared to the wool dyeings.

It is well known that silk is a natural protein fiber consisting of various amino acids like wool. However, different compositions of the amino acids between wool

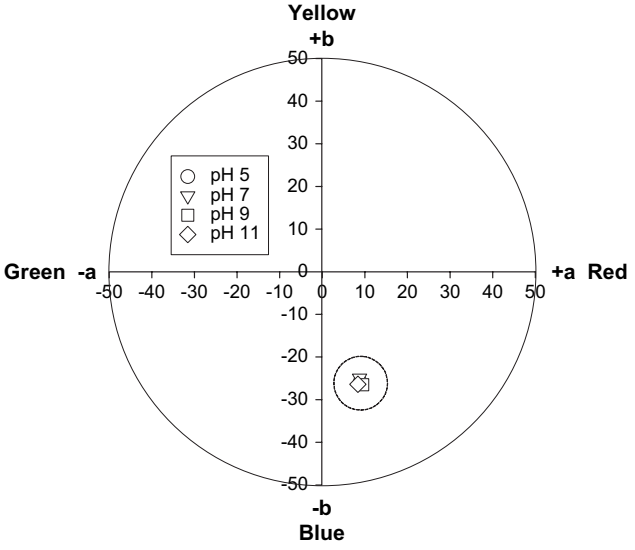


Fig. 6. Color coordinates of silk dyeings with C.I. Acid Blue 113 at various pHs.

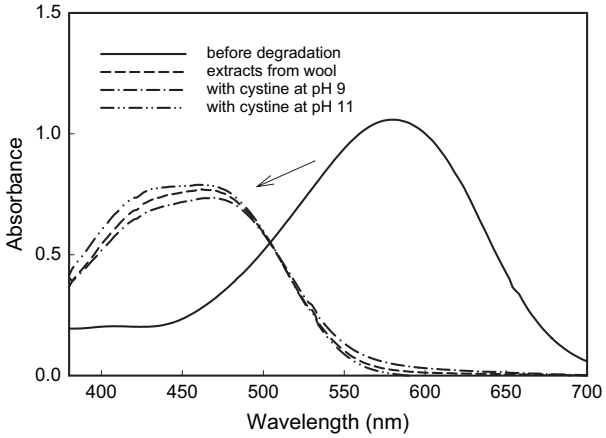


Fig. 7. UV/vis spectra of C.I. Acid Blue 113 before and after treatment with cystine in alkaline conditions.

and silk are of importance to understand the different dyeing properties. Wool keratins contain the specific sulfur-containing amino acids, namely cystine (11.59%), cysteine (0.18%) and methionine (0.63%) [7–10]. These three amino acids are only present in the wool fibers and the sulfur-containing amino acids could play an important role in degrading the dyes. However, silk fibroins do not contain any sulfur-containing amino acids. In this context, the degradation behaviors of C.I. Acid Blue 113 in the presence of these sulfur-containing amino acids were compared to the wool dyeings in the following experiment.

3.4. Model study of the dye degradation behaviors in the presence of sulfur-containing amino acids

Three sulfur-containing amino acids were used as model compounds to study the degradation behaviors of the C.I. Acid Blue 113. These amino acids were added into the dye baths using buffer systems of pH 9 and 11.

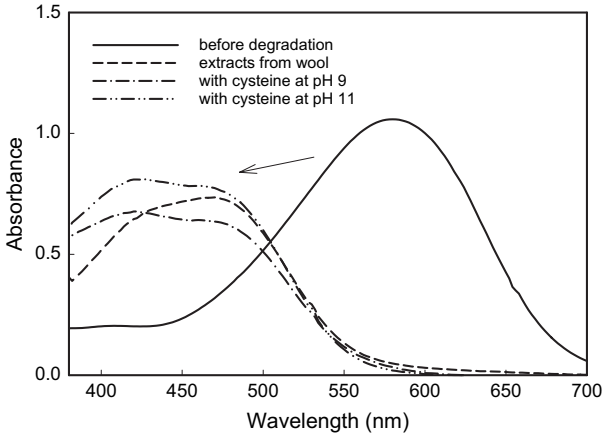


Fig. 8. UV/vis spectra of C.I. Acid Blue 113 before and after treatment with cysteine in alkaline conditions.

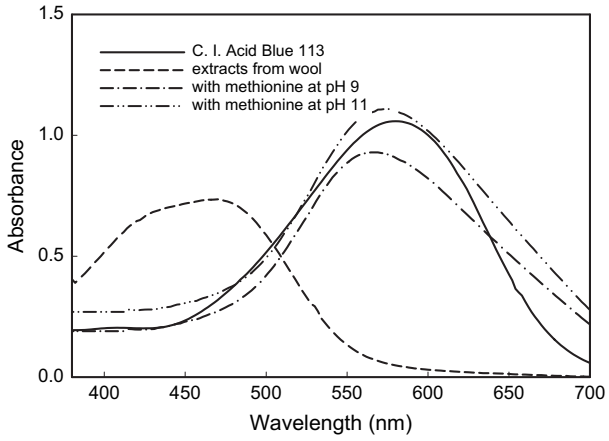


Fig. 9. UV/vis spectra of C.I. Acid Blue 113 before and after treatment with methionine in alkaline conditions.

The solutions were heated up to 95 °C and the treatments were continued for 60 min.

Figs. 7–9 show the UV/vis spectra of the dye solutions treated with cystine, cysteine, and methionine, respectively. As shown in Figs. 7 and 8, the dye solutions treated with cystine and cysteine at pH 9 and 11 showed very similar absorption spectra to the extracts from the color changed wool dyeing. The maximum absorption wavelength was shifted from 580 nm to 450 nm. However, the dye solution in the presence of methionine did not impart any change in the absorption wavelength (Fig. 9).

In addition, to confirm the degraded dye moiety, the solutions treated with cystine and cysteine were analyzed using the LC/MS. The mass spectra of the moieties treated with cystine and cysteine are shown in Figs. 10 and 11, respectively.

In Figs. 10 and 11, the m/z 326.1 was predominantly detected. It was the same result as the previous finding from wool dyeing, which was the moiety having one azo group. This result was attributable to the reductive degradation of the disazo group within the dye molecule. Because the degraded dye moiety still has one azo

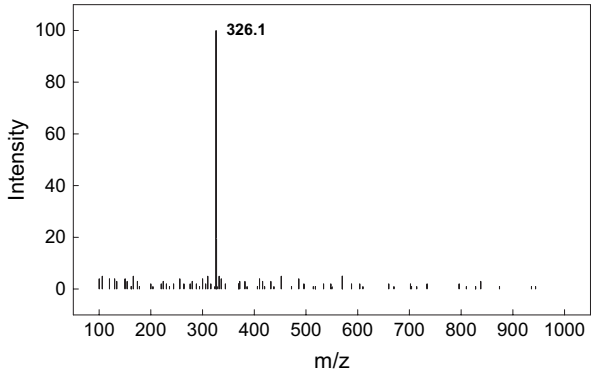


Fig. 10. Mass spectrum of the dye fragment of C.I. Acid Blue 113 degraded by treatment with cystine.

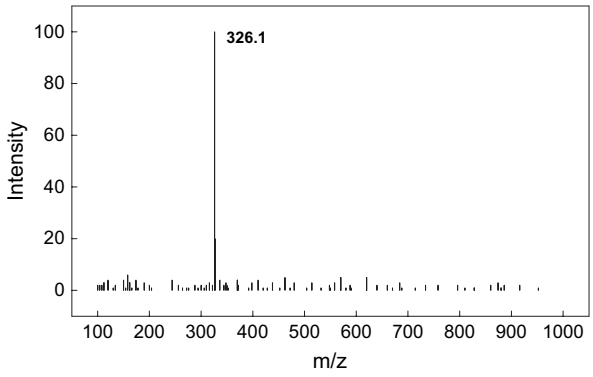
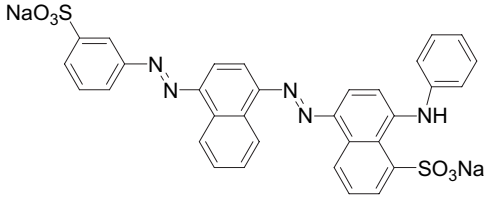


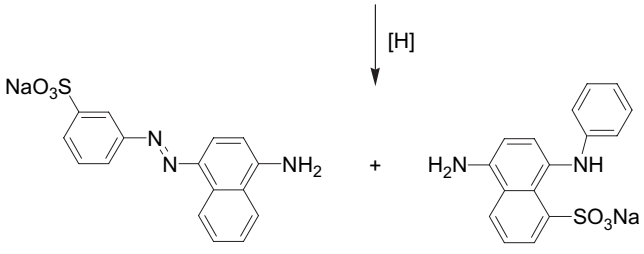
Fig. 11. Mass spectrum of the dye fragment of C.I. Acid Blue 113 degraded by treatment with cysteine.

group, it shows reddish orange color to be like other commercial monoazo dyes.

It is well known that the natural protein fibers such as wool and silk are susceptible to alkali. When wool fibers are treated with alkali, the fiber molecules are gradually damaged. Also the amino acids decomposed from the wool fibers could be dissolved into the treatment solutions. The disulfide linkages (−S−S−) of the cystines were slowly cleaved and converted into the cysteines containing thiol groups (−SH). These thiol groups can be reversibly reformed back to the cystines [11,12]. These thiol groups release hydrogen radicals that are very reductive chemical species. In this context, the reason for the disazo dye degradation could be explained as follows. The cystines in wool fibers were cleaved into cysteine groups during the dyeing process. The cysteines released the hydrogen radicals during reversibly reforming back to the cystines and these active hydrogen radicals reduced



C. I. Acid Blue 113 (Nave blue color)



Orange color Colorless

Fig. 12. Degradation of C.I. Acid Blue 113 caused by reducing effect of the cystines and the cysteines.

the azo group in the dye molecule, which caused the color changes of the wool dyeings (Fig. 12). Moreover, a series of degradation reaction were accelerated in alkaline conditions, because more amino acids from wool molecules were dissolved into the dyeing solutions.

4. Conclusions

In order to investigate the color change of the disazo acid dyes in wool dyeing, C.I. Acid Blue 113 was used and its color change was studied. The dye degradation was attributed to the reducing effect of the sulfur-containing amino acids of wool fibers.

The dye showed its original navy blue color in acidic and neutral dyeing conditions, but in alkaline baths its color changed to reddish orange. From the model study using cystine and cysteine, it was obvious that the disazo dye was degraded into the monoazo moiety due to the reducing effect of the cystines and the cyteines.

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